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# THERMODYNAMIC PROPERTIES OF DIFLUOROMETHANE ON THE SATURATION CURVE

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## ABSTRACT

Vapor pressures in the range of 256 to 331 K and saturated liquid and vapor densities from 315 to 331 K have been measured for difluoromethane (HFC-32) on the saturation line by means of variable volume and static experimental methods. Our results have been combined with literature values, and on the basis of all the measurements, accurate analytical correlations for saturated liquid and vapor densities and vapor pressures have been established. The functional form of the correlations is accurate over a wide range of temperatures including those near the critical temperature. The uncertainty in these correlations are comparable to uncertainties in the experimental data on which the correlations are based. Comparisons of thermodynamic properties on the saturated line, calculated using these correlations, with generalized correlations for HFC-32 reported earlier are also discussed.

## INTRODUCTION

Hydrofluorocarbon (HFC) compounds have received much attention as replacement working fluids for refrigeration processes due to their low ozone depletion and global warming potentials. HFC refrigerants are also attractive because of their higher energy efficiency, which reduces of their total global warming impact. However, no single HFC compound has been identified as a replacement for the widely used refrigerants, HCFC-22 and R-502 [1,2]. Alternatively, a number of binary and ternary mixtures containing HFC-32 as a constituent have been identified as potential replacements. Pure difluoromethane is not a feasible working fluid because of its high flammability and vapor pressure, but this HFC can form azeotropic and near-azeotropic mixtures with other compounds and has a higher efficiency than most other alternatives. Therefore, HFC-32 as an added constituent will improve the energy efficiency of refrigerant blends. In the present paper, we combine our measurements of vapor-liquid equilibrium (VLE) for HFC-difluoromethane with data available in the literature to provide thermodynamic properties for this HFC over a wide range of temperatures, induding those in the vicinity of the critical point.

## EXPERIMENTAL RESULTS

Two different experiments have been used to measure the thermodynamic properties of difluoromethane at saturation. A static method was applied to measure vapor pressures. In this method, a 75 $cm^3$ stainless steel cell was immersed in a Neslab temperature bath which controls temperature to 0.01 K. The temperature of the bath was measured to the same accuracy using a resistance thermometer. The equilibrium cell was connected by stainless steel tubing to one side of a Ruska differential pressure cell (Model 2413-705). The vapor pressure on this side of the differential cell was balanced by nitrogen pressure using a Ruska differential pressure null indicator (Model 2416-711). Nitrogen pressure was controlled and measured to an accuracy of 0.001 MPa with a Heise Precision pressure controller (Model PPC-159). The differential pressure cell, connecting lines, and valves were heated to at least 5 K higher than the bath temperature to ensure no condensation of the vapor phase. Further details of the apparatus and experimental technique are given elsewhere [3].

Vapor pressures have been measured at thirty-two temperatures between 255.95 and 291.21 K. Experimental uncertainties in the temperature are less than ±0.02 K, and the maximum uncertainty in pressure is less than 0.2% of the measured value at the lowest pressure. The purity of the sample was 99.95%. The measured vapor pressures are summarized in Table 1.

Table 1. Experimental vapor pressures of difluoromethane

| $T$, K | $P$, MPa | $T$, K | $P$, MPa | $T$, K | $P$, MPa | $T$, K | $P$, MPa |
|---|---|---|---|---|---|---|---|
| 255.95 | 0.4512 | 259.81 | 0.5193 | 267.74 | 0.6824 | 280.47 | 1.0230 |
| 255.98 | 0.4514 | 261.18 | 0.5447 | 268.17 | 0.6923 | 281.13 | 1.0436 |
| 256.02 | 0.4529 | 263.69 | 0.5942 | 270.14 | 0.7387 | 282.91 | 1.1006 |
| 256.04 | 0.4532 | 264.42 | 0.6100 | 270.59 | 0.7500 | 285.42 | 1.1851 |
| 256.13 | 0.4548 | 265.21 | 0.6267 | 272.60 | 0.8025 | 285.97 | 1.2045 |
| 256.17 | 0.4550 | 265.82 | 0.6397 | 273.26 | 0.8176 | 287.89 | 1.2734 |
| 256.62 | 0.4625 | 266.12 | 0.6462 | 275.89 | 0.8884 | 289.21 | 1.3221 |
| 258.96 | 0.5034 | 267.47 | 0.6762 | 279.01 | 0.9784 | 291.21 | 1.3988 |

Vapor pressures, and saturated liquid and vapor densities of difluoromethane have been also measured using a variable volume apparatus with a molibden-glass view cell. This apparatus and the experimental technique have been reported earlier [4] and discussed in detail elsewhere [5]. The measured properties of difluoromethane (99.80% pure) at saturation is given in Table 2 for temperatures between 280.15 and 331.14 K.

Table 2. Experimental vapor pressure, saturated liquid and vapor densities of difluoromethane

| $T$, K | $P$, MPa | $\rho'$, kg m$^{-3}$ | $\rho''$, kg m$^{-3}$ |
|---|---|---|---|
| 280.15 | 1.0086 | - | - |
| 298.03 | 1.6782 | - | - |
| 315.02 | 2.5795 | 884.9 | 76.6 |
| 323.14 | 3.1331 | 841.1 | 97.7 |
| 331.14 | 3.7525 | 791.0 | 125.8 |

Experimental uncertainties in the temperature was estimated to be ±0.015 K. The experimental uncertainties in pressure was 0.1 - 0.2%, liquid density - 0.15 - 0.25%, vapor density - 0.25 - 0.35%.

## DATA SOURSES AND CALCULATIONS

Table 3 list the saturation conditions and the number of data points that were used in the correlating the thermodynamic properties of difluoromethane.

Table 3. Summary of experimental data used in the correlations for difluoromethane

| Authors, year | Ref. number | Number of data points | Temperature range, K | Pressure range, MPa | Density range, kgm$^{-3}$ |
|---|---|---|---|---|---|
| Vapor pressure | | | | | |
| Malbrunot et al., 1968 | 6 | 30 | 191-351 | 0.016-5.83 | - |
| Adams and Stein, 1971 | 7 | 4 | 222-283 | 0.105-1.11 | - |
| Kanungo et al., 1987 | 8 | 11 | 149-245 | 0.0003-0.29 | - |
| Baroncini et al., 1993 | 9 | 56 | 238-351 | 0.22-5.75 | - |
| Weber and Goodwin, 1993 | 10 | 27 | 208-237 | 0.049-0.21 | - |
| Widiatmo et al., 1994 | 11 | 25 | 220-325 | 0.095-3.28 | - |
| Bouchot and Richon, 1994 | 12 | 8 | 253-334 | 0.4-3.95 | - |
| Türk et al., 1994 | 13 | 27 | 204-351 | 0.04-5.83 | - |
| Fukushima et al., 1995 | 14 | 57 | 277-351 | 0.93-5.74 | - |
| Oguchi et al., 1995 | 15 | 16 | 243-351 | 0.27-5.75 | - |
| This work* | - | 5 | 280-331 | 1.01-3.75 | - |
| This work** | - | 32 | 256-291 | 0.45-1.39 | - |
| Saturated liquid density | | | | | |
| Malbrunot et al., 1968 | 6 | 15 | 248-349 | - | 113-575 |

Table 3. (Continued)

| Authors, year | Ref. number | Number of data points | Temperature range, K | Pressure range, MPa | Density range, $kgm^{-3}$ |
|---|---|---|---|---|---|
| Shinsaka et al., 1985 | 16 | 20 | 150-222 | - | 1204-1385 |
| Widiatmo et al., 1994 | 11 | 22 | 220-322 | - | 797-1209 |
| Sato et al., 1994 | 17 | 2 | 321-344 | - | 675-850 |
| Oguchi et al., 1995 | 15 | 5 | 255-293 | - | 981-1115 |
| This work* | - | 3 | 315-331 | - | 791-885 |
| Saturated vapor density | | | | | |
| Bouchot and Richon, 1994 | 12 | 4 | 253-313 | - | 11-73 |
| Fukushima et al., 1995 | 14 | 5 | 310-336 | - | 67-151 |
| This work* | - | 3 | 315-331 | - | 78-126 |

* - Obtained by variable volume method.
** - Obtained by static method.

The functional forms chosen for fitting the vapor pressures, and the saturated liquid and vapor densities [18] are, respectively,

$$\ln(P_c / P_s) = a\ln(T_c / T) + b\left(\ln(T_c / T)\right)^c \quad (1)$$

$$\ln(\rho' / \rho_c) = B_1\left(\ln(T_c / T)\right)^{\beta F_1(\tau)} \quad (2)$$

$$\ln(\rho_c / \rho'') = B_2\left(\ln(T_c / T)\right)^{\beta F_2(\tau)} \quad (3)$$

where $\tau=\ln(T_C/T)$; $a$, $b$, $c$, $B_1$, $B_2$, $\beta$ are the fitted coefficients, which depend on the specific properties of difluoromethane; and $F_1(\tau)$, $F_2(\tau)$ are the following universal crossover functions,

$$F_1(\tau)=1-1.113\tau^{0.4}/\ln\tau \quad (4)$$

$$F_2(\tau)=1+4.82\tau^{0.6}/\ln\tau \quad (5)$$

The critical parameters for difluoromethane used in Eqs. (1) - (3) were determined on the basis of data reported in the literature (Table 4). Initially, we determined average values of the critical parameters weighted by their standard deviations and values for the average standard deviation using the data in Table 4. These parameters were then used in Eqs. (1) - (3) to obtain an optimal set of critical parameters using the data from this work. The critical properties for difluoromethane that were used in the present calculations and the coefficients in Eqs. (1) - (3) are given in Table 5.

Table 4. Summary of critical properties measurements for difluoromethane

| Authors, year | Ref. number | Critical temperature, K | Critical density, $kg\ m^{-3}$ | Critical pressure, MPa | Purity, % |
|---|---|---|---|---|---|
| Malbrunot et al, 1968 | 6 | 351.54±0.2 | 430 | 5.830 | 99.85 |
| Smith and Srivastava, 1986 | 19 | 351.0 | - | - | - |
| Singh et al., 1991 | 20 | 351.56±0.02 | 429.61 | 5.814 | - |
| Nishimura et al., 1992 | 21 | - | - | 5.780±0.002 | 99.98 |
| Fukushima and Ohotoshi, 1993 | 22 | 351.26±0.03 | 425±5 | 5.778±0.003 | 99.98 |
| Holcomb et al., 1993 | 23 | - | 428.50±1.83 | - | 99.9 |
| Jelinek and Daltrophe, 1993 | 24 | 351.55 | 429.6 | - | - |
| Grebenkov, 1993 | 25 | 351.55 | 421.1 | 5.843 | - |
| Schmidt and Moldover, 1994 | 26 | 351.36±0.02 | 419±7 | 5.7927±0.024 | 99.9 |

Table 4. (Continued)

| Authors, year | Ref. number | Critical temperature, K | Critical density, kg $m^{-3}$ | Critical pressure, MPa | Purity, % |
|---|---|---|---|---|---|
| Higashi, 1994 | 27 | 351.26±0.01 | 427±5 | 5.785±0.009 | 99.98 |
| Kuwabara et al., 1994 | 28 | 351.255±0.01 | 424±1 | - | 99.998 |
| Sato et al., 1994 | 16 | - | - | 5.784±0.0025 | 99.9 |
| Türk et al., 1994 | 14 | 351.23±0.06 | 420±8 | 5.783±0.06 | 99.98 |

Table 5. Critical properties and coefficients in Eqs. (1) - (3)

| | |
|---|---|
| $T_c$, K | 351.255 |
| $P_c$, MPa | 5.784 |
| $\rho_c$, kg $m^{-3}$ | 424 |
| $a$ | 7.26622 |
| $b$ | 5.53976 |
| $c$ | 2.686 |
| β | 0.32475 |
| $B_1$ | 1.75095 |
| $B_2$ | 2.30530 |

## DISCUSSION

Deviations of the calculated properties using Eqs. (1) - (3) from the experimental data (Table 3) do not exceed 0.5% for vapor pressure, 0.4% for saturated liquid and 1.3% for saturated vapor density over entire range of temperatures investigated.

Eqs. (1) - (3) are also in satisfactory agreement with other correlations reported earlier [29, 30] as shown by the comparisons in Figs. 1, 2, and 4. Deviations in vapor pressures (Fig. 4) over the temperature range from 250 K to the critical temperature is less than 1%. Similar systematic deviations in vapor pressure at low temperatures are due to experimental data used to develop the vapor pressure correlation [29, 30], which did not include data by Malbrunot et al. [6] and Kanungo [8] at temperature from 191 to 350 K and 149 to 245 K, respectively.

The present calculations of saturated liquid density are in a good agreement with previous calculations [29, 30] at all temperatures except near the critical point (Fig. 2). In these previous works, multiple-term scaling-type equations for saturated liquid density were chosen. It should be noted that the critical index, β, used in [29] and [30] was 0.355 and 0.3, respectively is much different than the theoretically estimated value of β=0.3245 and the value in Table 5 of β=0.32475. In this case, using β=0.32475 with a universal crossover function that approaches 1 as the temperature approaches the critical temperature, gives an adequate description of the experimental data over a wide range of conditions including those in a vicinity of the critical point : $t=1-T/T_c<0.1$.

Taking into account that the liquid density measurements are more reliable and have a higher accuracy than the vapor density measurements, we used the same value of β in Eq.(3) for calculating the vapor densities of difluoromethane. The accurate description of measured liquid and vapor densities using Eqs.(2) and (3), respectively, and their predictive ability in the vicinity of the critical region are shown in Fig. 3 by comparing these calculations with the two independent Wagner-type correlations developed by Kuwabara et al. [28] and Higashi [27] on the basis of their own data near the critical point. In spite of the fact that experimental data in the critical region was not included in developing our Eqs.(2) and (3) (due to difficulties determining the phase boundary accurately in the vicinity of the critical point), Fig.3 shows very good agreement with the other correlations: within 1.5% for the saturated liquid densities and 2.5% for the saturated vapor densities.

Fig.4 is a plot of deviations in saturated vapor densities of HFC-32 using Eq. (3) by [29] and [30]. In one case [30], the calculated saturation densities were obtained on the basis of an equation of state that had been developed without

the experimental dew point curve. As a result, those results show deviations on the order of 4 - 6% higher that our results at overlapping temperatures. The saturated vapor density data used by Outcalt and McLinden [29] included the data of Defibaugh et al. [31]. The deviations in saturated vapor densities calculated in this case are less than 2% over temperatures from 260 to 350 K, which is less than experimental uncertainties of the data along the saturation curve. Limitations to the application of Eq.(3) are determined by its functional form, which allows describing vapor densities over a the wide range of condition in the critical region, but does not give a smooth transition to an ideal gaseous state at $T/T_C<0.65$ and $\rho<10\text{-}20$ kg m$^{-3}$.

## CONCLUSION

Basis on measurements of the saturated thermodynamic properties, which includes our own data and experimental results from the literature, accurate correlations for vapor pressure, and saturated liquid and vapor densities of difluoromethane were developed. The functional forms of the correlations are simple, have only a few terms, and allow the prediction of these thermodynamic properties for difluoromethane along the saturation curve over wide temperature range and in the vicinity of the critical point.

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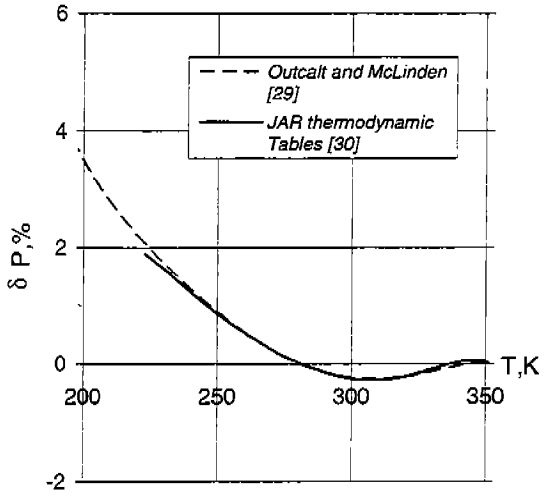


Fig.1 Deviation of vapor pressure of HFC-32 from Eq.(1)

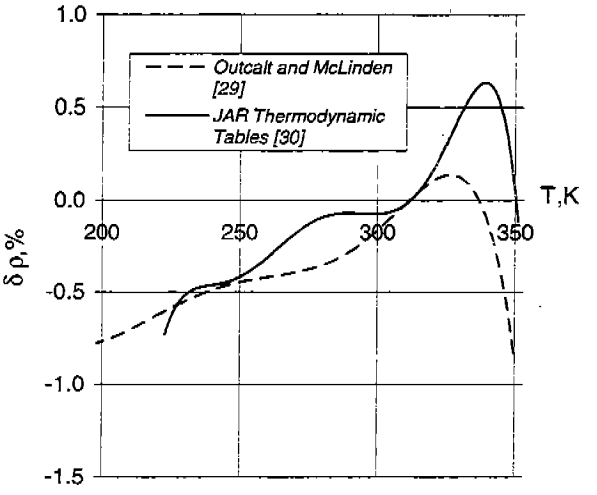


Fig.2 Deviation of saturated liquid densities of HFC-32 from Eq.(2)

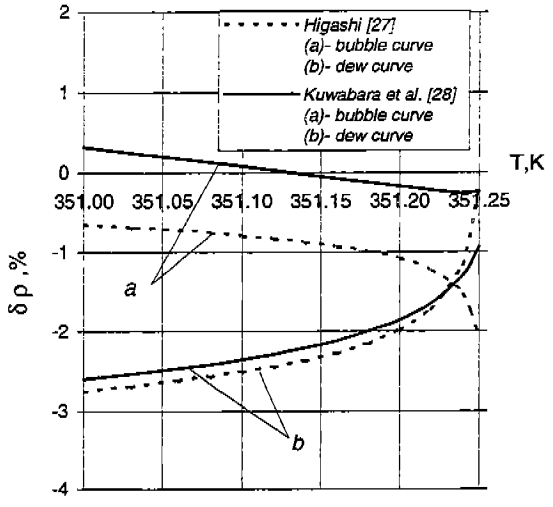


Fig.3 Deviation of saturated liquid and vapor densities of HFC-32 from Eqs.(2) and (3)

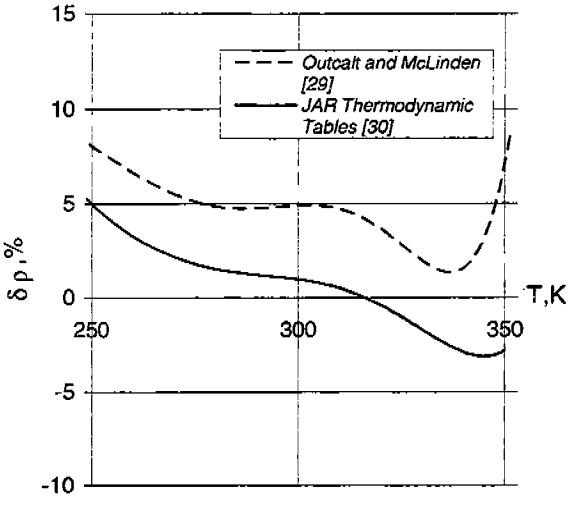


Fig.4 Deviation of saturated vapor densities of HFC-32 from Eq.(3)